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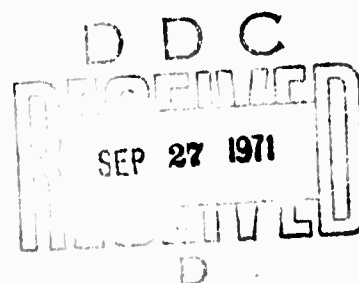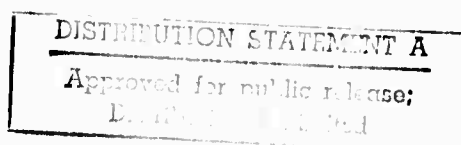# First Semi-Annual Technical Report, 1971
# The Structure of Non-Crystalline Materials

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THE STRUCTURE OF NON-CRYSTALLINE MATERIALS

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# STRUCTURE DETERMINATION OF AMORPHOUS

# Ge, GeO$_2$ AND GeSe BY FOURIER ANALYSIS OF

# EXTENDED X-RAY ABSORPTION FINE STRUCTURE (EXAFS)[*]

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## Abstract

Fourier inversion of EXAFS data is a powerful new technique for structural investigation of non-crystalline materials with the unique capability to determine the near neighbor environment of each type of atom in a complex material. The radial structure function so obtained contains information on the number, distance to, and distribution of atoms surrounding the absorbing atom. The data on Ge and GeO2 generally agree with previous findings but with added detail. The environment of both Ge and Se in amorphous GeSe show a significant change from the crystalline material with evidence for local satisfaction of the directed bonding tendencies of each atomic species.

## 1. Introduction

This paper describes the application of a new technique for structural determination to the amorphous semiconductors Ge, $GeO_2$, and GeSe. The EXAFS technique is based upon the sensitivity of the fine structure observed on the high energy side of an x-ray absorption edge to the short range order around the absorbing atom and has the unique capability to determine the local atomic environment of each different kind of atom in a complex material. A theory of EXAFS based upon the interaction of the ejected photoelectron with the atoms surrounding the absorbing atom, has been given[1] in which the dominant term for the oscillatory part of the absorption coefficient is[2]

$$\chi(k) = - kf(k) \sum_j \frac{N_j \exp(-\gamma r_j)}{r_j^2} \exp(-\sigma_j^2 k^2/2) \sin\left(2kr_j + 2\eta(k)\right) \tag{1}$$

where k is the wavevector of the ejected photoelectron, f(k) is the electron scattering factor, $r_j$ is the distance from the absorbing atom to the $j^{th}$ coordination shell, $N_j$ is the number of atoms at $r_j$, $\exp(-\gamma r_j)$ is a photoelectron range term, $\exp(-\sigma_j^2 k^2/2)$ is a temperature term and $\eta(k)$ is the phase shift of the photoelectron caused by the potential of the absorbing atom. Although eq. (1) was originally derived assuming cubic symmetry[1], it can be shown that this result is valid for any atomic symmetry.

This expression may be formally inverted using Fourier analysis to obtain a radial structure function, $\phi(r)$, which is given by[2]

$$\phi(r) = - \sqrt{\frac{2}{\pi}} \int_0^\infty \chi(k) k^{-1} f(k)^{-1} \sin\left(2kr + 2\eta(k)\right)$$

$$= \frac{1}{2} \sum_j \frac{N_j \exp(-\gamma r_j)}{r_j^2 \sigma_j} \exp[-2(r-r_j)^2/\sigma_j^2] \tag{2}$$

The right hand side of eq. (2) shows that the transform of the experimentally observed function, $\chi(k)$, is a series of normal gaussians centered at each $r_j$ with structurally significant position, amplitude and width; i.e., it is possible to determine the number of atoms at $N_j$ and their distributions about $r_j$. Specifically, when $r = r_j$ the amplitude $A_j$ of the peak can be used to determine $N_j$ from

$$A_j = \frac{N_j \exp(-\gamma r_j)}{2 r_j^2 \sigma_j}, \quad W = \sqrt{2}\,\sigma \quad (3)$$

and the full width, $W$, at $A_j/e$ determines $\sigma_j$, the mean amplitude of the relative displacement from the absorbing atoms of the atoms in the $j^{th}$ shell including both thermal and disorder contributions.

Since neither the experimental data nor the theory is in terms of an absolute absorption coefficient, the data analysis in this paper is accomplished by comparing the amorphous material to its crystalline polymorph for which the range parameter, phase shift and thermal smearing may be determined experimentally and which should be nearly identical if the short range order is similar.

The integration in eq. (2) is made over a finite range so that the Fourier inversion introduces broadening of the peaks and a termination ripple which complicates the data analysis. (See Warren[3] and Kaplow, et al.[4] for a discussion.) The presence of these effects negates possible structural data from the widths of the gaussians (improved data processing being developed will remove this limitation); therefore, structural information given herein is in terms of the positions and amplitudes of the coordination peaks.

## 2. Experimental

The absorption edge and EXAFS is obtained on an automated x-ray spectrometer.[5] The final data are the average of ten experiments in order to reduce

the statistical noise to less than ≈ 0.1%. After a computer filtering program which separates the fine structure spectrum from the sloping absorption edge and the statistical noise the integration of eq. (2) is done numerically. Examples of EXAFS are given in Fig. 1. The data for the crystalline material was similar but with more fine detail.

Amorphous Ge and GeSe were prepared by evaporation from a tungsten boat in a vacuum of at least $10^{-5}$ torr onto substrates of mylar or aluminum foil to a thickness of about 1μ. The problem of non-stoichiometric sublimation of GeSe was recognized[6] and since a multiple furnace technique was not available various sized pieces of GeSe were sublimed simultaneously. Measurements of the relative x-ray absorption coefficients proved that the resultant films were within 3% of equiatomic composition. Glassy $GeO_2$ was prepared by melting the hexagonal form of $GeO_2$ in a quartz tube and quenching into water. All materials were examined by x-ray diffraction. The crystalline samples gave the expected patterns and the amorphous samples each had a characteristic pattern of broad smooth peaks with no sign of crystallinity.

### 3. Radial Structure Curves

In Fig. 2, the radial structure function of amorphous and crystalline Ge is compared. The two curves are plotted on a slightly different vertical scale for comparison; however, only the relative amplitudes normalized to the 1st peak height of each type of Ge will be compared. The rapid decrease in coordination peak amplitude with increasing r is a consequence of the $1/r^2$ and $\exp(-\gamma r)$ dependence. We have chosen to plot this type of radial structure function, rather than the usual radial distribution function, in order to more clearly illustrate the r dependence of the EXAFS transform.

In crystalline Ge the first six shells are clearly resolved. Since $N_j$, $r_j$, and $\sigma_j$ are known for crystalline Ge the range parameter $\gamma$ may be determined from the measured amplitude $A_j$ using eq. (3) where we have calculated $\sigma$ as in ref. 1.

The value determined by plotting $\log \left( A_j / (N_j / 2\sigma_j r_j^2) \right)$ vs. r is $\gamma = .31 A^{-1}$ which corresponds to a meanfree path for scattering into an eigenstate of $1/\gamma = 3.2 A$. Since the short range structure of crystalline and amorphous Ge are similar we assume that the same value of $\gamma$ applies to amorphous Ge. This is a critical assumption since there is no other way to determine $\gamma$ for an amorphous material. This technique was also used to determine $\gamma$ from crystalline $GeO_2$ and GeSe.

The amorphous Ge data shows that the first two peaks are at the crystalline distances while the third peak, such as it is, is shifted from the third crystalline distance. This is consistent with the radial distribution functions of Shevchik[7] for Ge, and of Moss and Graczyk[8] for Si and also with the model calculation by Polk.[9] In principle the width of the gaussians allows determination of $\sigma_j$ and, then with the previously determined $\gamma$, $N_j$ is calculated from the height. However, the quality of the present data permits only a relative comparison of the amorphous (A) and crystalline (C) Ge 2nd coordination shell. We find using eq. (3) that

$$\sigma^2(A) \approx 6\sigma^2(C) \tag{5}$$

Assuming the temperature contribution to be the same, this is a disorder smearing of $\approx 0.15 A$. Since this atomic distance is along the edge of the tetrahedron it means that the tetrahedral bond angles are distorted $\pm 5°$ Amorphous Ge is consistent with the model of a continuous random network of slightly distorted tetrahedra.

Fig. 3 compares glassy (G) and crystalline (hex) $GeO_2$ with a Ge atom at the origin. (Instrumental capability did not permit investigation of the oxygen absorption edge.) Both curves have been normalized to unity at the first peak. The vertical lines indicate the atom positions in $GeO_2$-hex and their amplitudes have been calculated from eq. (3) assuming $\sigma$ to be the same for all shells. The difference in scattering factors between Ge and O was approximately accounted for by assuming that each factor was proportional to the number of electrons, $f_{Ge} = 4f_0$. Relative to $GeO_2$-hex the 1st peak which is the tetrahedral Ge-O bond moves in slightly to 1.60Å vs. 1.65Å. The 2nd peak which is the Ge-Ge distance of adjacent tetrahedra decreases to 3.07Å vs. 3.14Å. The 25% decrease in peak amplitude can be attributed to a proportionate decrease in number of atoms or disorder smearing or both. The 3rd $GeO_2$-G peak at 3.85Å is significantly different from $GeO_2$-hex and could be due to 1 Ge atom or 4 oxygen atoms. Since this distance is greater than that possible for Ge-Ge in adjacent, oxygen-sharing tetrahedra it is tentatively identified with the median oxygen atoms in adjacent tetrahedra and suggests that the alignment of oxygen atoms is more symmetric (like the β-cristobalite structure) in $GeO_2$-G than in $GeO_2$-hex. Generally, these results are in agreement with the x-ray scattering results of Zarzycki[10] and the x-ray absorption study of Nelson, Siegel and Wagner;[11] however, these results surpass others in resolution and detail.

Figs. 4 and 5 compare crystalline and amorphous GeSe in the neighborhood of both Se and Ge atoms and illustrate the power of the EXAFS technique to probe the structure around individual atomic species. As in Fig. 3 the lines represent the positions of the atoms in the crystalline material relative to a Se atom in Fig. 4 and a Ge atom in Fig. 5, with the amplitudes

calculated from eq. (3) ignoring possible differences in the $\sigma$'s. The atomic arrangement is a highly distorted NaCl structure[12] with each atom having 6 neighbors of the opposite kind (3 at ~2.58Å and 3 at ~3.33Å); however, beyond the second neighbors the structures around Ge and Se differ. A comparison of the crystalline data in Figs. 4 and 5 proves that these differences are clearly in evidence and that the experimental data agree well with the known structure. In the amorphous data the near neighbor arrangement shows a striking change from crystalline GeSe. The first peak splits into two peaks at 2.35 and 2.80Å. There is a small peak remaining at the second crystalline distance in both cases, and beyond that the structures appear to be different. The similarity of the amorphous data in Figs. 4 and 5 also indicates that the amorphous material was primarily GeSe and not phase separated Ge and Se since the pure Ge structure as shown in Fig. 2 can not be seen in the data.

In order for the theory to determine the absolute number of atoms in each peak a qualitative comparison of the oscillation amplitude in the EXAFS spectra between the crystalline and amorphous structures was made which indicates a total of three atoms at the near neighbor distances in the amorphous material and this is reasonable considering the starting material. Using this comparison we normalize the amorphous GeSe (and SeGe) radial structure functions to 2 atoms at 2.35Å and find the other atom at 2.80Å. Since a Ge-Se covalent bond is 2.37Å it appears that in going from the crystalline to the amorphous material the material has changed from a more to less distorted covalent bonding arrangement for the nearest neighbors. This splitting is more clearly resolved around the Se atom and may illustrate the tendency of Se to link two nearby Ge atoms into a chain as the other nearby

Ge atom is forced away. The tendency of Ge to form tetrahedrally directed bonds may result in the less well resolved splitting of Fig. 5. A satisfactory structural unit incorporating these features and satisfying all bonding requirements has not yet been visualized.

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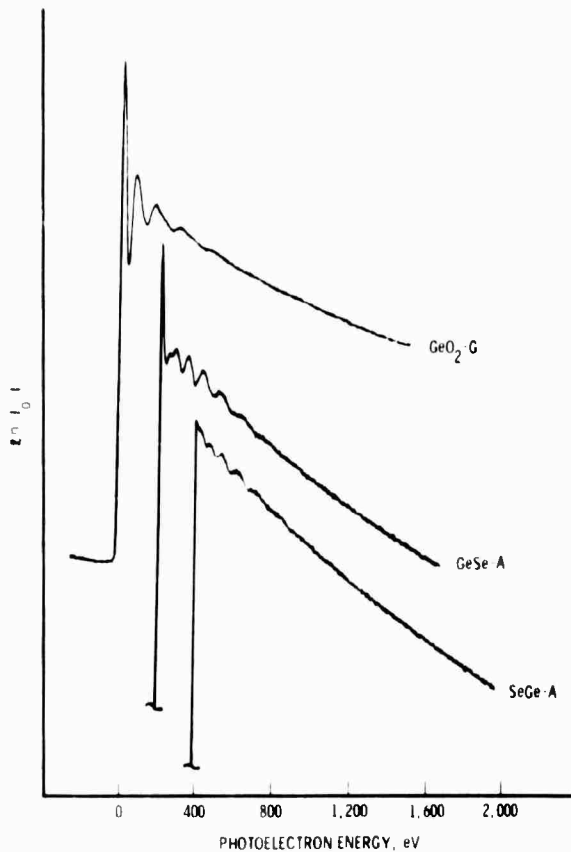12. R. W. G. Wyckoff, Crystal Structures , 2nd Ed., Vol. 1, (Interscience, New York, 1963).

Fig. 1  Examples of EXAFS for amorphous
materials. (The amorphous Ge
data is contained in Ref. 2.)
$GeO_2$-G and GeSe-A are the Ge K
X-ray absorption edge. SeGe-A
is the Se K X-ray absorption
edge. The two lower curves are
displaced downward and to the
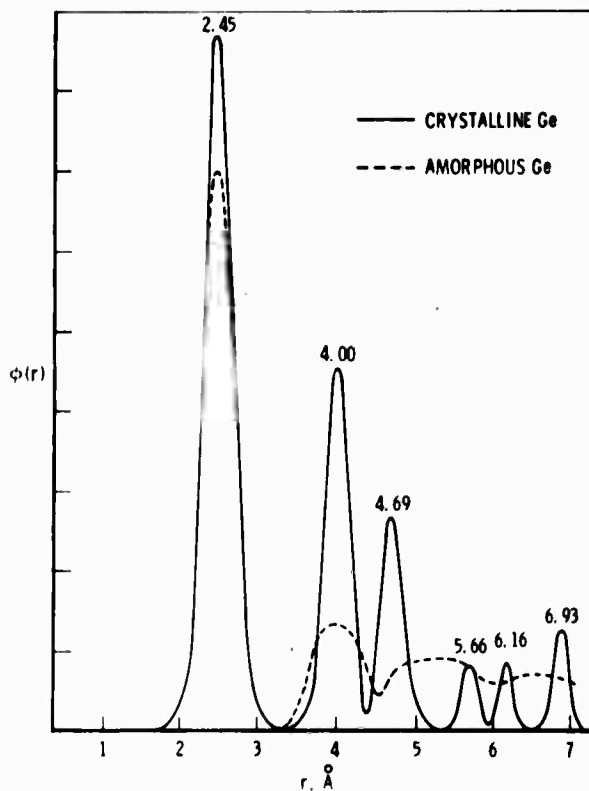right for clarity.



Fig. 2  Radial structure curves for
amorphous and crystalline Ge.
Numbers over the peaks indicate
the distance to each coordina-
tion shell in crystalline Ge.
The vertical error bar ($\pm 1\sigma$) in
Figs. 2-5 was estimated by
replicate analysis. The error
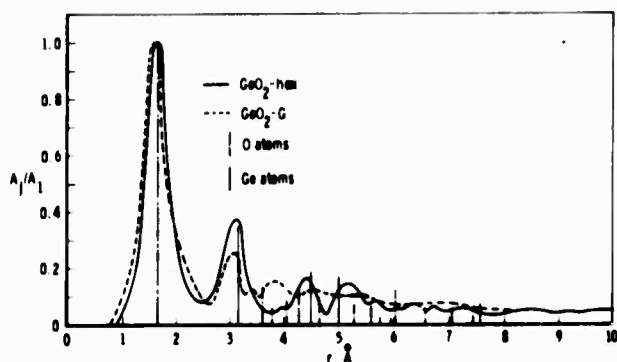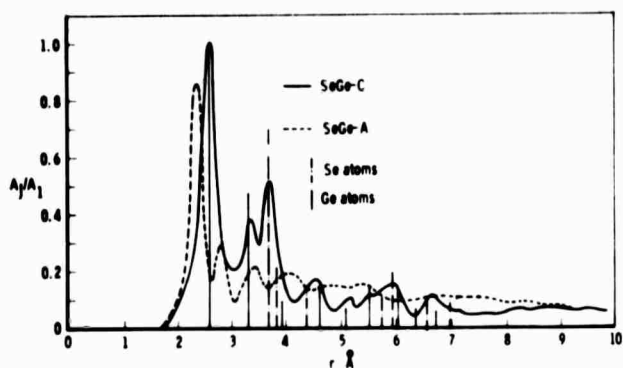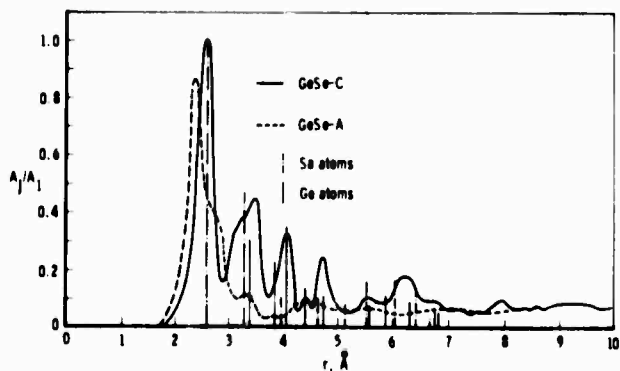on r was $\pm 1\%$.

**Fig. 3.**



**Fig. 4.**



**Fig. 5.**



**Figs. 3-5.** Radial structure curves for amorphous and crystalline $GeO_2$ and GeSe. The solid and dashed lines indicate the crystalline and amorphous materials, respectively. Vertical lines indicate the amplitude predicted by Eq. (3) and are keyed to each kind of atom. Fig. 4 and Fig. 5 illustrate the environment in GeSe of Se and Ge atoms, respectively.